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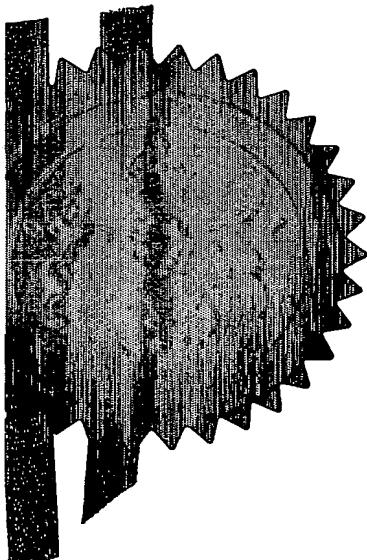
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1. Your reference

SMC 60630/GB/P

2. Patent application number

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0326997.4

20 NOV 2003

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Aveca Limited
Hexagon House
Blackley
Manchester, M9 8ZS
United Kingdom
07764137001

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

GB

4. Title of the invention

COMPOUNDS

5. Name of your agent (if you have one)

MAYALL, John

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Aveca Limited
Hexagon House
Blackley
Manchester, M9 8ZS
United Kingdom

Patents ADP number (if you know it)

9244313002

6244313004

If you are claiming priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country	Priority application number (if you know it)	Date of filing (day / month / year)
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Number of earlier application	Date of filing (day / month / year)
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Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
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Description

17

Claim(s)

02

Abstract

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Statement of inventorship and right to grant of a patent (Patent Form 7/77)

Request for preliminary examination and search (Patent Form 5/77)

Request for substantive examination
(Patent Form 10/77)

Any other documents
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1 cover sheet

11.

I/We request the grant of a patent on the basis of this application.

Signature *C. Shepherd*. Date 20/11/03
Avecla Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K.M. Pinder/Mrs G. Shepherd 0161 721 1361/2

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COMPOUNDS

This invention relates to compounds suitable for use as dyes, to inks and to their use in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

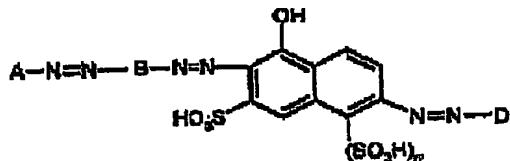
There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, ozone-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

JP10195320 describes dyes including tris-azo dyes carrying a pyrazolyl azo group and their use in the coloration of paper and pulp.

US patent application 2001/0027734 describes metal complexes of tris-azo dyes derived from tris-azo molecules optionally containing a (substituted) pyrazolylazo moiety. The copper complexes are said to be particularly preferred.

We have surprisingly found that certain non-metallised compounds provide valuable colorants for ink jet printing inks.

According to the present invention there is provided a compound of Formula (1) or salt thereof:



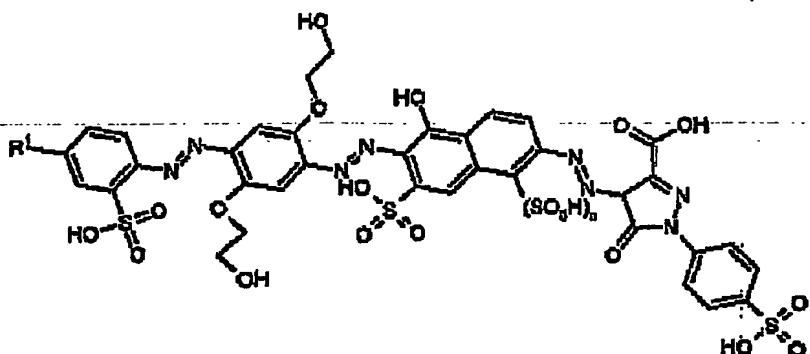
Formula (1)

wherein:

- 25 A is optionally substituted phenyl or naphthyl;
- B is optionally substituted phenylene or naphthylene;
- n is 0 or 1;
- D is a pyrazolyl group; and

wherein the compound of Formula (1) is not of Formula (2) or a salt thereof:

2



Formula (2)

wherein:

R¹ is C₁₋₄ alkyl or C₁₋₄ alkoxy; and

n is 0 or 1.

Preferably A is optionally substituted phenyl.

Preferably B is optionally substituted phenylene. The optional substituents which may be present on A or B are preferably selected from hydroxy, halo, nitro, cyano, carboxy, sulpho, phosphato, optionally substituted amino (especially amino or amino carrying one or more C₁₋₄-alkyl groups), optionally substituted acylamino (especially C₁₋₄-acylamino or phenylacetylamino, each of which optionally carries a sulpho or a carboxy group), optionally substituted ureido (especially ureido or ureido carrying one or two C₁₋₄-alkyl groups), optionally substituted C₁₋₆-alkyl, optionally substituted C₁₋₆-alkoxy, optionally substituted C₁₋₆-alkylthio, optionally substituted aryl, optionally substituted C₁₋₆-alkylsulphonyl and optionally substituted sulphonamido (especially sulphonamido or sulphonamido carrying one or two C₁₋₄-alkyl groups). Preferably A carries at least one water-solubilising group selected from carboxy, sulpho and phosphato.

As examples of optionally substituted phenyl and naphthyl groups represented by A there may be mentioned 4-amino-2,5-disulphophenyl, 2-sulpho-4-methoxyphenyl, 2-carboxy-4-sulphophenyl, 2-sulpho-4-methyl and 2-sulpho-4,5-dimethylphenyl.

In one aspect of the present invention there is provided a compound of Formula (1) with the proviso that when A is optionally substituted phenyl, A is free from nitro groups.

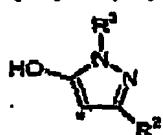
The optional substituents on B are preferably selected from carboxy, sulpho, phosphato, optionally substituted amino, acylamino, optionally substituted ureido, optionally substituted alkyl, optionally substituted alkoxy and optionally substituted aryl.

When B is substituted phenylene it preferably carries one or more groups selected from optionally substituted C₁₋₆-alkyl, optionally substituted C₁₋₆-alkylthio, optionally substituted C₁₋₆-alkoxy, optionally substituted amino, optionally substituted ureido, carboxy

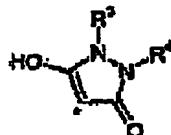
and sulphato. When B is optionally substituted naphthylene the naphthylene ring preferably carries one or more water solubilising groups, more preferably by one or two groups selected from carboxylic, sulphonic and phosphonic acid groups.

As examples of optionally substituted phenylene and naphthylene groups represented by B there may be mentioned 2,5-di(2-hydroxyethoxy)phen-1,4-ylene, 2,5-dimethoxyphen-1,4-ylene, 2,5-diethoxyphen-1,4-ylene, 2-methoxy-5-aminophen-1,4-ylene, 2-methoxy-5-acetylaminophen-1,4-ylene.

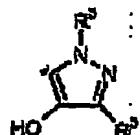
Preferably D is a pyrazolyl group carrying at least one carboxy, sulfo or phosphato group. In an especially preferred embodiment, D is a pyrazolaryl group of Formula (3a), (3b) or (3c):



Formula (3a)



Formula (3b)



Formula (3c)

wherein

R² and R³ are each independently H, carboxy, cyano or optionally substituted alkyl, alkoxy, acyl, aryl, amino, amido, carbonamido, carboxyester, sulphamoyl or alkylsulphonyl; and

R³ and R⁴ are each independently H or optionally substituted aryl or alkyl; where the asterisk * shows the point of attachment to the azo linkage in Formula (1).

R² is preferably an optionally substituted C₁₋₆-alkyl, C₁₋₆-acyl or amino group or a group capable of hydrogen bonding in the free acid form with the adjacent azo group such as carboxy. More preferably R² is carboxy.

Preferred optionally substituted C₁₋₆-alkyl groups are optionally substituted C₁₋₄-alkyl, more preferably C₁₋₄-alkyl which is unsubstituted or carries a halo atom or a carboxy, sulpho or phosphato group.

Preferred optionally substituted C₁₋₆-alkoxy groups are optionally substituted C₁₋₄-alkyl, more preferably C₁₋₄-alkyl which is unsubstituted or carries a halo atom or a carboxy, sulpho or phosphato group.

Preferred optionally substituted phenyl groups are those mentioned above for A.

Preferred optionally substituted sulphonamide groups are of the formula SO₂NR⁶R⁷ wherein R⁶ and R⁷ are each independently H, optionally substituted C₁₋₆ alkyl.

Preferred optionally substituted amino groups are optionally substituted acylamino, especially C₁₋₄-acylamino, more preferably optionally substituted ureido which is unsubstituted or carries a carboxy, sulpho or phosphato group.

Preferably acyl groups are optionally substituted C₁₋₄alkylacyl, optionally substituted phenylacyl, preferably acetyl or benzoyl.

Preferred substituents which may be present on the optionally substituted C₁₋₄alkyl, C₁₋₄alkoxy, C₁₋₄alkylthio, aryl (especially phenyl), C₁₋₄alkylsulphonyl substituents on any of A, B, R², R³, R⁴, R⁵, R⁶ and R⁷ are selected from hydroxy, halo, nitro, cyano, carboxy, sulpho, phosphato, acylamino, ureido, C₁₋₄alkyl, C₁₋₄alkoxy, C₁₋₁₀alkylthio, aryl, C₁₋₄alkylsulphonyl and sulphonamido.

As examples of groups represented by R² there may be mentioned methyl, carboxy and H.

R³ and R⁴ are preferably each independently an optionally substituted aryl group, more preferably phenyl or naphthyl carrying one or two substituents selected from carboxy or sulpho.

As examples of groups represented by R³ and R⁴ there may be mentioned 4-sulphophenyl and 2-sulphoniaphthyl.

R⁵ is preferably carboxy or a C₁₋₄alkylcarboxyester.

In view of the above preferences, in a preferred embodiment:

A Is phenyl carrying one or two substituents selected from carboxy, sulpho, phosphato, amino, methyl, methoxy and acetamido;

B Is phenylene or naphthylene carrying one or two substituents selected from sulpho, methyl, methoxy and 2-hydroxyethoxy;

n Is 0 or 1;

D Is of Formula (3a), (3b) or (3c);

R² Is H, methyl or carboxy;

R³ and R⁴ are each independently phenyl or naphthyl carrying one or two substituents selected from sulpho and carboxy; and

R⁵ is a C₁₋₄alkylcarboxyester.

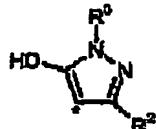
In a further preferred embodiment:

A Is phenyl carrying one or two substituents selected from carboxy, sulpho, amino, methyl, methoxy and acetamido;

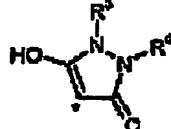
B Is phenylene or naphthylene carrying one or two substituents selected from sulpho, methyl and methoxy 2-hydroxyethoxy;

n Is 0 or 1;

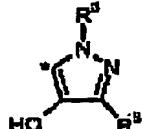
D Is of Formula (3a), (3b) or (3c);



Formula (3a)



Formula (3b)

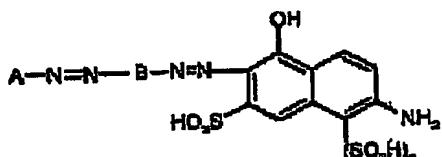


Formula (3c);

R^2 and R^5 are each independently H, carboxy, cyano or optionally substituted alkyl, alkoxy, acyl, aryl, amino, amido, carbonamido, carboxyester, sulphamoyl or alkylsulphonyl; and

R^3 and R^4 are each independently H or optionally substituted aryl or alkyl;

where the asterisk * shows the point of attachment to the ezo linkage in Formula (1).
The compounds of Formula (1) may be prepared by diazotising a compound of the Formula (4) wherein n, A and B are as hereinbefore defined to give a diazonium salt and coupling the resultant diazonium salt with a compound of Formula H-D wherein D is as hereinbefore defined:



Formula (4).

The diazotisation is preferably performed at a temperature of 0°C to 10°C. Preferably the diazotisation is performed in water, preferably at a pH below 7. Dilute mineral acid, e.g. HCl or H₂SO₄, may be used to achieve the desired pH conditions.

The compound of Formula (4) may be prepared by diazotising a compound of Formula A-N=N-B-NH₂ to give a diazonium salt and coupling the resultant diazonium salt with 1-hydroxy-3-sulpho-6-aminonaphthylene optionally carrying a sulpho group at the 5-position; wherein A and B are as hereinbefore defined. Reaction conditions are those generally used in the dyestuff art, for example as described in for example EP 0356080.

When the compound of Formula (1) is in the form of a salt the preferred salts are alkali metal salts (especially lithium, sodium and potassium salts), ammonium and substituted ammonium salts and mixtures thereof. Especially preferred salts are sodium, potassium and lithium salts, salts with ammonia and volatile amines and mixtures thereof. The lithium salts have good solubility, forming particularly storage stable links with low toxicity and no tendency to block ink jet nozzles.

The compounds may be converted into a desired salt using known techniques. For example, an alkali metal salt of a compound may be converted into the ammonium or substituted ammonium salt by dissolving an alkali metal salt of the compound in water, acidifying with a mineral acid and adjusting the pH of the solution to pH 9 to 9.5 with ammonia or the amine and removing the alkali metal cations by dialysis or by use of an ion exchange resin.

Examples of amines which may be used to form such salts include methylamine, dimethylamine, trimethylamine, ethylamine, n-propylamine, iso-propylamine, n-

butylamine, iso-butylamine, sec-butylamine, tert-butylamine, piperidine, pyridine, morpholine, allylamine, diethylamine, triethylamine, tetramethyl amine and mixtures thereof. It is not essential that the dyes are completely in the form of the ammonium salt or substituted ammonium salt and mixed alkali metal and either ammonium salt or substituted ammonium salt are effective, especially those in which at least 50% of the cations are ammonium or substituted ammonium ions.

Still further salts are those with the counter ions described in US 5830265, claim 1, Integer (b), which are included herein by reference thereto.

The compounds of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present claims.

In a second aspect of the present invention there is provided a composition which comprises a compound of Formula (1) as hereinbefore defined and a liquid medium, wherein the liquid medium comprises water and an organic solvent.

A preferred composition according to the second aspect comprises:

- (a) from 0.01 to 30 parts of a compound of Formula (1) or salt thereof; and
- (b) from 70 to 99.99 parts of a liquid medium;

wherein the liquid medium comprises an organic solvent and all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts. Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates which may be used to prepare inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media comprise water and an organic solvent, preferably in a weight ratio of water to organic solvent of 99:1 to 1:99, more preferably 99:1 to 50:50 and especially 95:5 to 80:20.

It is preferred that the organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol,

hexylene glycol and thioglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-soluble organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thioglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially ((2-methoxy-2)-ethoxy)-2-ethoxyethanol.

The compounds of the invention may be used as the sole colorant in inks because of their attractive black shade. However, if desired, one may combine the present compounds with one or more further colorants if a slightly different shade is required for a particular end use. The further colorants are preferably dyes. When further colorants are included in the ink these are preferably selected from black, magenta, cyan and yellow colorants and combinations thereof.

Suitable further black colorants include C.I.Food Black 2, C.I.Direct Black 19, C.I.Reactive Black 31, PRO-JET™ Fast Black 2, C.I.Direct Black 195; C.I.Direct Black 168; and black dyes described in patents by Lexmark (e.g. EP 0 539,178 A2, Example 1, 2, 3, 4 and 5), Orient Chemicals (e.g. EP 0 347 803 A2, pages 5-6, azo dyes 3, 4, 5, 6, 7, 8, 12, 13, 14, 15 and 16) and Seiko Epson Corporation.

Suitable further magenta colorants include PRO-JET™ Fast Magenta 2.

Suitable further cyan colorants include phthalocyanine colorants, C.I. Direct Blue 199 and C.I. Acid Blue 99.

Suitable further yellow colorants include C.I.Direct Yellow 142; C.I.Direct Yellow 132; C.I.Direct Yellow 86; C.I.Direct Yellow 85; C.I. Direct Yellow 173; and C.I.Acid Yellow 23.

The ink may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, migration reducing additives and surfactants which may be ionic or non-ionic.

The pH of the composition is preferably from 4 to 11, more preferably from 7 to 10.

The viscosity of the composition at 25°C is preferably less than 50cP, more preferably less than 20 cP and especially less than 5cP.

When the compositions according to the second aspect of the invention are used as ink jet printing compositions, the composition preferably has a concentration of halide ions of less than 500 parts per million, more preferably less than 100 parts per million. It is especially preferred that the composition has less than 100, more preferably less than 60 parts per million of divalent and trivalent metals, wherein parts refer to parts by weight relative to the total weight of the composition. We have found that purifying the composition is to reduce the concentration of these undesirable ions reduces nozzle blockage in ink jet printing heads, particularly in thermal ink jet printers. A further aspect of the invention provides a process for printing an image on a substrate comprising applying thereto a composition according to the second aspect of the present invention to the substrate by means of an ink jet printer.

The ink jet printer preferably applies the composition to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the composition in a reservoir by means of a resistor adjacent to the orifice, thereby causing the composition to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the composition from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably a treated substrate such as a coated paper or coated plastic, especially coated paper.

Preferred plain or treated papers are papers which may have an acid, alkaline or neutral character. Examples of commercially available treated papers include HP Premium Coated Paper, HP Photopaper (both available from Hewlett Packard Inc.); Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (all available from Seiko Epson Corp.); Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 and HG201 High Gloss Film and Canon PR101 (all available from Canon).

A further aspect of the present invention provides a paper, an overhead projector slide or a textile material printed with a composition, a compound or by means of a process as hereinbefore defined.

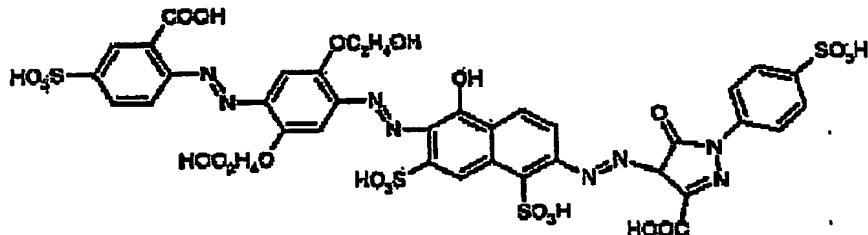
A still further aspect of the present invention provides an ink jet printer cartridge, optionally refillable, comprising one or more chambers and a composition, wherein the composition is present in at least one of the chambers and the composition is as defined in the second aspect of the present invention.

The present compounds and compositions provide prints of attractive, neutral black shades which are particularly well suited for the ink jet printing of text and images. The compositions have good storage stability and low tendency to block the very fine nozzles used in ink jet printers. Furthermore, the resultant images have excellent optical density, shade, light-fastness, wet-fastness, humidity fastness and resistance to fading in the presence of oxidising air pollutants.

The Invention is further illustrated by the following Examples in which all parts and percentages are by weight unless specified otherwise.

10 Example: 1

Preparation of:



Stage A

15 : 5-Sulphoanthranilic acid (44.4g, 92.56g@100%) was dissolved in water (500ml) by adjusting the pH to 8-9 with lithium hydroxide solution (2M) and sodium nitrite (11.4g) added. The solution was then added to a stirred mixture of ice & water containing concentrated hydrochloric acid (50ml). The reaction was further stirred for 1 hr at 0-10°C after which time excess nitrous acid was destroyed by addition of sulphamic acid.

20 A solution of 2,5-bis-(2-acetoxyethoxy)aniline (44.55g) in acetone (500ml) was added to the above prepared diazonium salt solution before stirring overnight allowing to self warm to room temperature. The product was isolated by filtration, washed with water, slurried in acetone (1.5litres) and again isolated by filtration before drying at 50°C. Yield = 82.5g.

25 Stage B

The product from Stage A (28g) was suspended in N-methylpyrrolidone (250ml) and sodium nitrite (7.5g) added. After stirring for 10mins at room temperature a solution of concentrated hydrochloric acid (16ml) in water (100ml) was slowly added during which time the temperature rose to 45°C. The reaction mixture was stirred for 2hrs allowing to self-cool to room temperature and excess nitrous acid destroyed by the adding sulphamic acid.

6-Amino-1-naphthol-3,5-disulphonic acid (20g) was dissolved in water (200ml) by adjusting the pH to 8-9 with lithium hydroxide solution (2M). The above prepared diazonium salt solution was then slowly added at 0-10°C maintaining the pH at 7-8 by addition of lithium hydroxide solution (2M) as necessary. After stirring for 1hr lithium hydroxide (10g) was added and the reaction mixture stirred for a further 1hr at room temperature at which time thin layer chromatography showed the hydrolysis to be complete. The pH was adjusted to 7 by addition of concentrated hydrochloric acid and lithium chloride solution (50% w/v) added. After self cooling to room temperature the product was isolated by filtration and washed with lithium chloride solution (50% w/v).

5 The product was purified by dissolving in water (200ml) and re-precipitating with acetone (2.5litres). The acetone was removed by decantation and the residue dissolved in water to give a solution that was found, by titration with titanous chloride, to contain 0.05 mole of product. The product was used in Stage C without further purification.

10

15 **Stage C - Title Dye**

The product from Stage B was stirred at room temperature and sodium nitrite (3.8g) and Calsolene™ oil (1g) added. The mixture was then added to a stirred mixture of ice & water containing concentrated hydrochloric acid (20ml). Stirring was continued for 2hrs at 0-10°C during which time the diazonium salt precipitated from solution as a suspension. A solution of 1-(4-sulphophenyl)-3-carboxypyrazol-5-one (15.5g) dissolved in water (200ml) and the pH adjusted to 7-8 by addition of lithium hydroxide solution (2M) was added to the diazonium salt suspension and stirring was continued for 1hr at 0-10°C maintaining the pH at 7-8 by addition of lithium hydroxide solution (2M) as necessary. The product was isolated by drown out into acetone (5litres) and subsequent filtration. The crude product was purified by dissolution in water (300ml) and repeating the drown out into acetone (2.5litres). After filtration the product was dissolved in water and dialysed to low conductivity and finally isolated by evaporation to dryness at 70°C. Yield = 46.3g.

20

25

Examples 2-9

30 The method of Example 1 was repeated except that in Stage A the 5-sulphoanthranilic acid was replaced with an amine of formula corresponding to the structure in column A of Table 1; where indicated by n=0, the 6-amino-1-naphthol-3,5-disulphonic acid was replaced with 6-Amino-1-naphthol-3-sulphonic acid; and in Example 9, Stage C, the 1-(4-sulphophenyl)-3-carboxypyrazol-5-one was replaced by the pyrazole of formula D as indicated in Table 1. The structure of the resultant compound is also shown in Table 1.

35

Table 1

	λ_{max} (nm)		
Final dye structure	604 nm 70,200		
	594 nm 54,200		
	588 nm 66,100		
D			
n	0	0	
A	<chem>SC(=O)c1ccc(N)cc(O)S(=O)(=O)C</chem>	<chem>CC1=CNC=C1C(=O)N2C=CC=C2S(=O)(=O)C</chem>	
EX	2	3	4
	<chem>SC(=O)c1ccc(N)cc(O)S(=O)(=O)C</chem>	<chem>CC1=CNC=C1C(=O)N2C=CC=C2S(=O)(=O)C</chem>	<chem>CC1=CNC=C1C(=O)N2C=CC=C2S(=O)(=O)C</chem>
	<chem>SC(=O)c1ccc(N)cc(O)S(=O)(=O)C</chem>	<chem>CC1=CNC=C1C(=O)N2C=CC=C2S(=O)(=O)C</chem>	<chem>CC1=CNC=C1C(=O)N2C=CC=C2S(=O)(=O)C</chem>
	<chem>SC(=O)c1ccc(N)cc(O)S(=O)(=O)C</chem>	<chem>CC1=CNC=C1C(=O)N2C=CC=C2S(=O)(=O)C</chem>	<chem>CC1=CNC=C1C(=O)N2C=CC=C2S(=O)(=O)C</chem>

Table 1 Continued

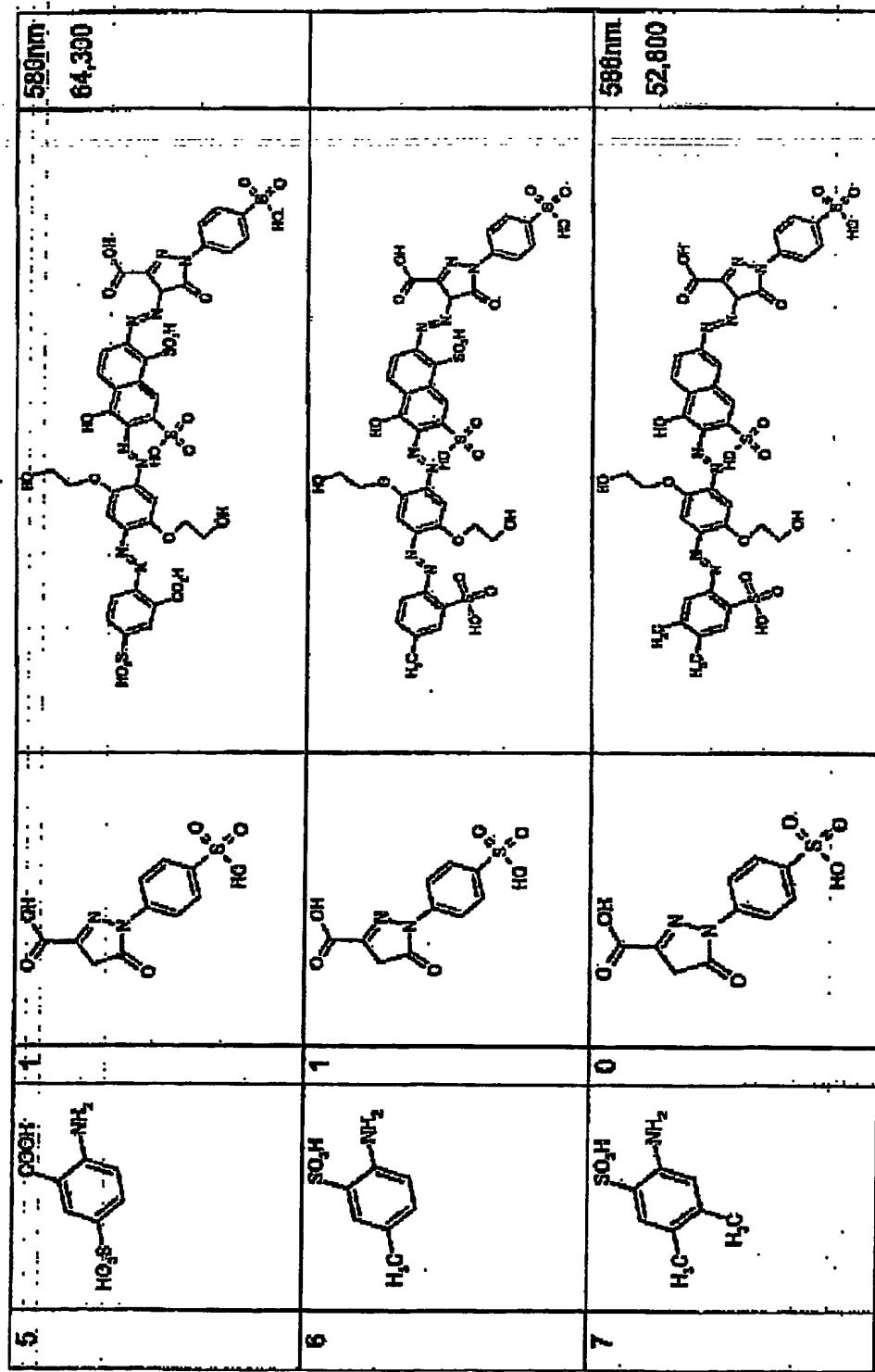
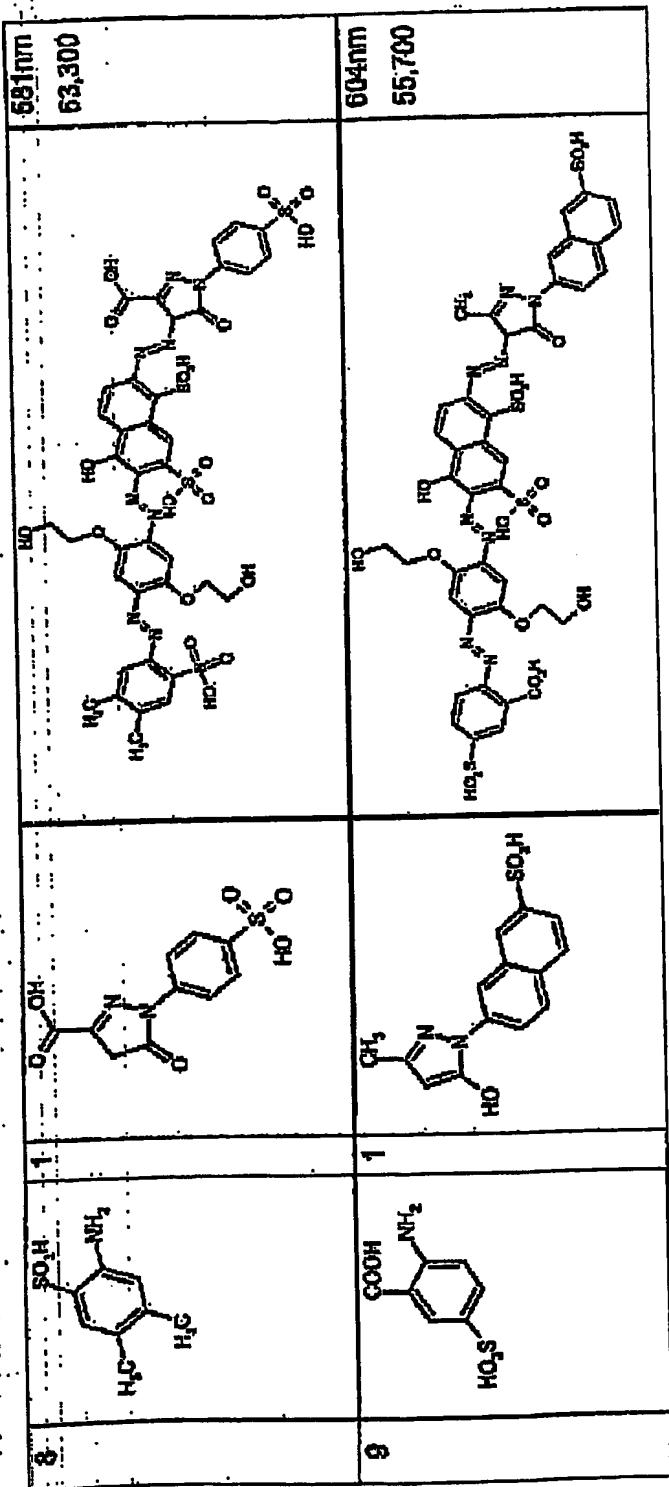


Table 1 Continued



Example 10 - Inks

Inks may be prepared containing the dyes from Example 1 to Example 9 according to the following formulation:

5	2-Pyrrolidone	5 parts
	TGlycol	5 parts
	Surfynol™ 4651 part	
	Dye	3 parts
	Water	amount required to make up to 100 parts

Surfynol™ 465 is a surfactant available from Air Products and Chemicals Inc., USA.

10 Further inks may be prepared according to Tables 2 and 3 wherein the dye described in the first column is the dye made in the above example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

15 The following abbreviations are used in Tables 2 and 3:

20	PG = propylene glycol
	DEG = diethylene glycol
	NMP = N-methyl pyrrolidone
	DMK = dimethylketone
	IPA = isopropanol
	MEOH = methanol
	2P = 2-pyrrolidone
	MIBK = methylisobutyl ketone
	P12 = propane-1,2-diol
25	BDL = butane-2,3-diol
	CET = cetyl ammonium bromide
	PHO = Na ₂ HPO ₄ and
	TBT = tertiary butanol
30	TDG = thiodiglycol

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SMG 60630
N-02 9259800

15.

Example 11 - Ink Jet Printing

The inks prepared in Example 10 may be incorporated into an empty cartridge of a Hewlett Packard DeskJet 550C™ ink jet printer and printed onto e.g. Xerox X Acid™, Canon PR101 or Epson SEC PM paper to give prints of excellent optical density, shade, light and ozone fastness.

5

TABLE 2

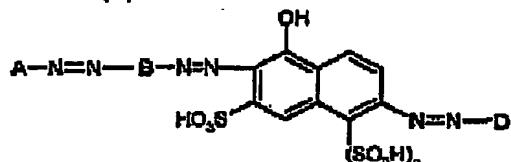
Dye	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	PA	MEOH	2P	MIBK
1	2.0	80.	5	6	6	4	0.2		5	1	5	
2	3.0	90	85	3	6	3	3		9	5	9	
3	10.0	85	91	5	6	9	0.5	4	5	6	15	
4	2.1	86	81	1.1	4	15	3	0.2	10	6	4	
5	3.1	60	60	2.5	60	3	3	0.5	6	4	6	
6	6	65	65	5	5	2	10	4	1	5	15	
7	7	75	75	4	4	5	5	0.3	4	4	2	
8	8	80	80	2.4	20	4	6		5	1	3	
9	9	89	89	4.1	15	5	10		6	6	5	
10	10	96	96	3.2	65	5	5		11	1	1	
11	1	90	90	5.1	80	2	2		10	7	0.3	
12	2	80	80	10.0	84	5	5		2	2	4	
13	3	84	84	1.8	80	2	2		7	1	3	
14	4	90	90	2.6	80	5	5		10	7	5	
15	5	80	80	3.3	80	2	2		2	2	4	
16	6	90	90	12.0	90	2	2		20	2	4	
17	7	68	68	6.4	68	2	2		2	3	5	
18	8	91	91	6.0	91	10	10		10	3	5	

TABLE 3

Dye	Dye Content	Water	PG	DEG	NMP	CET	TBT	TPO	BDL	PHQ	2P	P12
1	3.0	80	15									
2	9.0	90	5	5	5	0.2						
3	1.5	85	4	6	6	0.15	5.0	0.2				
4	2.5	90	8	8	8	0.3						
5	3.1	92	10	10	10	0.3						
6	0.9	85	5	5	5							
7	8.0	90	10	10	10							
8	4.0	70	4	4	4							
9	2.2	75	10	10	10							
10	10.0	91	6	6	6							
11	9.0	76	11	11	11							
12	5.0	78	5	5	5							
13	5.4	86	5	5	5							
14	2.1	70	10	10	10							
15	2.0	90	5	5	5							
16	2	88	2	2	2							
17	5	78	2	2	2							
18	6	70	5	5	5							
19	8	80	8	8	8							
20	10	80	10	10	10							
21	10	80	10	10	10							

CLAIMS

1. A compound of Formula (1) or salt thereof:



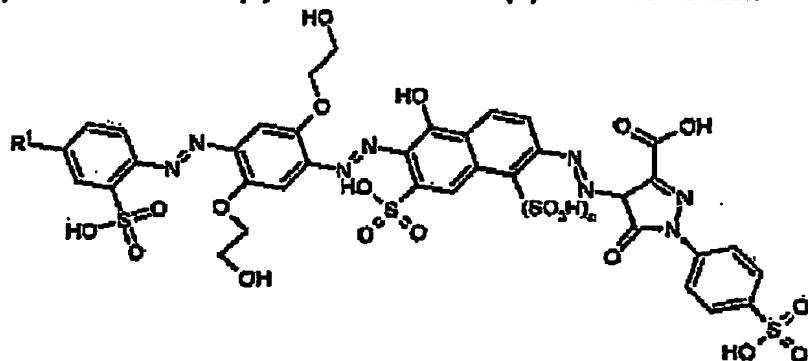
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Formula (1)

wherein:

- A : is optionally substituted phenyl or naphthyl;
- B : is optionally substituted phenylene or naphthylene;
- n : is 0 or 1;
- D : is a pyrazolyl group; and

wherein the compound of Formula (1) is not of Formula (2) or a salt thereof:



Formula (2)

15 wherein:

- R' : is C₁₋₄ alkyl or C₁₋₄ alkoxy; and
- n : is 0 or 1.

20 2. A compound according to claim 1 wherein D is a pyrazolyl group carrying at least one carboxy, sulpho or phosphonic acid group.

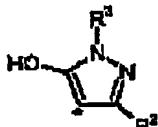
3. A compound according to any one of the preceding claims wherein:

- A : is phenyl carrying one or two substituents selected from carboxy, sulpho, amino, methyl, methoxy and acetamido.

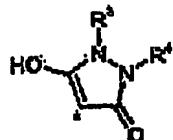
25 B : is phenylene or naphthylene carrying one or two substituents selected from sulpho, methyl and methoxy 2-hydroxyethoxy.

n is 0 or 1;

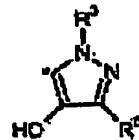
D is of Formula (3a), (3b) or (3c);



Formula (3a)



Formula (3b)



Formula (3c);

5 R² and R⁶ are each independently H, carboxy, cyano or optionally substituted alkyl, alkoxy, acyl, aryl, amino, amido, carbonamido, carboxyester, sulphamoyl or alkysulphonyl; and

R³ and R⁴ are each independently H or optionally substituted aryl or alkyl; where the asterisk * shows the point of attachment to the azo linkage in Formula (1).

10

4. A compound of Formula (1) as defined in claim 1, with the proviso that A is free from nitro groups when A is optionally substituted phenyl.

5. A compound according to any one of the Examples described herein.

15

6. A composition which comprises a compound of Formula (1) as defined in claim 1 and a liquid medium, wherein the liquid medium comprises water and an organic solvent.

20

7. A composition according to claim 6 which contains a further colorant selected from black, magenta, cyan or yellow colorants.

8. A process for printing an image on a substrate comprising applying thereto a composition according to any either of claims 6 or 7 by means of an ink jet printer.

25

9. A paper, an overhead projector slide or a textile material printed with a composition according to either of claims 6 or 7, a compound according to any one of claims 1 to 5, or by means of a process according to claim 8.

30

10. An ink jet printer cartridge, optionally refillable, comprising one or more chambers and a composition, wherein the composition is present in at least one of the chambers and the composition is according to either of claims 6 or 7.

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